

Catalytic Effect of a $\text{BH}_3:N,N$ -Diethylaniline Complex in the Formation of Alkenyl Catecholboranes from Alk-1-yne and Catecholborane

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Alkenyl catecholboranes are readily formed by the reaction of catecholborane and alk-1-yne at 25 °C, in the presence of 10 mol% of a $\text{BH}_3:N,N$ -diethylaniline complex, via a hydroboration–alkenyl transfer mechanism.

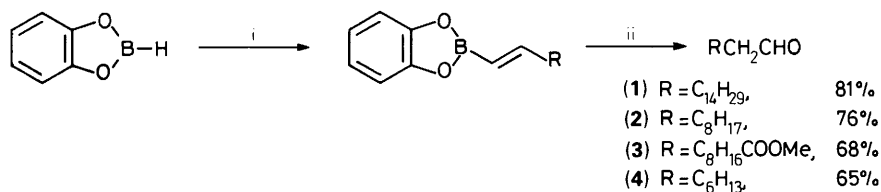
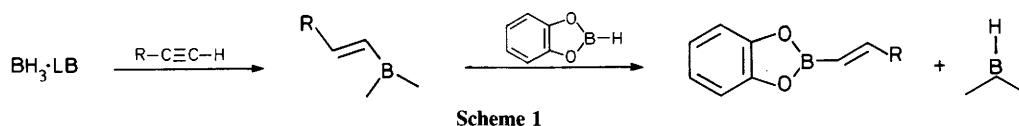
Catecholborane is a versatile reagent. Unfortunately, it only hydroborates alkenes and alkynes at elevated temperatures (70–100 °C).^{1–3} In recent years, there have been several reports on the catalysis of catecholborane hydroborations at 25 °C using transition metal complexes. For example, alkyl catecholboranes can be prepared from alkenes and catecholborane at ambient temperatures in the presence of the Wilkinson catalyst $(\text{Ph}_3\text{P})_3\text{RhCl}$ ⁴ and related reagents.⁵ We report that the alkenyl catecholboranes can be readily prepared in benzene at 25 °C in 24 h from catecholborane and alk-1-yne in the presence of 10 mol% of the $\text{BH}_3:N,N$ -diethylaniline complex, and converted into the corresponding aldehydes or alkenyl iodides in good yields.

In our studies on the development of new hydroborating agents,^{6–9} we were looking for more simple means for the ‘catalysis’ of catecholborane hydroboration. In 1971, it was reported that triaryloxyboranes exchange with trialkylboranes in the presence of a catalytic amount of $\text{BH}_3:\text{thf}$ (thf = tetrahydrofuran) at 100 °C to give the corresponding alkyl aryloxy borane derivatives $(\text{ArO})_2\text{BR}$.¹⁰ It was anticipated that since such disproportion reactions would most probably go through intermediates such as $(\text{ArO})_2\text{BH}$ and/or R_2BH species, hydroboration and exchange of the alkenyl/alkyl group with a diaryloxyborane such as catecholborane could be achieved as envisaged in Scheme 1.

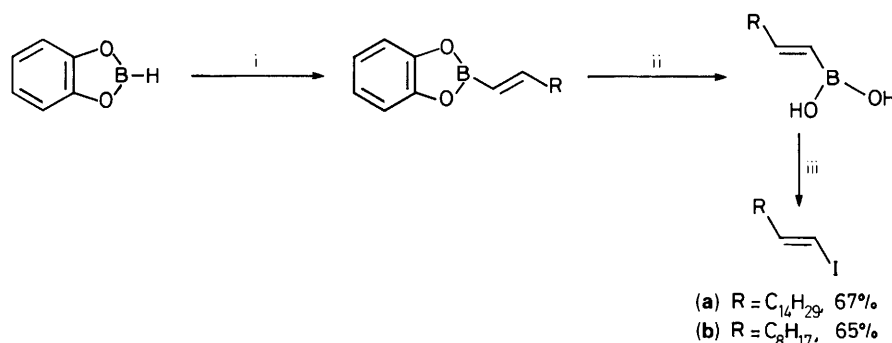
In order to examine this possibility, we have prepared catecholborane in benzene by passing B_2H_6 (25 mmol) into a suspension of catechol (10 mmol) in benzene at 25 °C. The resulting catecholborane was reacted with dec-1-ene (16 mmol) in the presence of a N,N -diethylaniline–borane complex (1 mmol) at 25 °C for 24 h; only 7.5% of decan-1-ol was isolated, which could have resulted from the hydroboration of dec-1-ene with the N,N -diethylaniline–borane complex. Clearly, a transfer reaction similar to the one shown in Scheme 1 does not take place in this case. However, when the alkene in the above experiment was replaced by alkynes (16 mmol), alkanals were obtained in 65–81% yields after oxidation with $\text{NaOAc}/\text{H}_2\text{O}_2$ ¹¹ (Scheme 2),^{†‡} which indicates that the

[†] The products were identified by spectral data (IR, ¹H NMR, ¹³C NMR) and comparison with the reported data. *Selected spectroscopic data*, ¹³C NMR (CDCl_3), for (1): δ 202.8, 43.9, 31.9, 29.7, 29.4, 29.1, 22.7, 22.0, 14.0. For (2): δ 202.7, 43.8, 31.7, 29.3, 22.5, 22.0, 13.9. For (3): δ 201.5, 173.3, 50.9, 33.6, 28.8, 28.6, 28.4, 28.2, 24.5, 18.0. For (a): δ 146.5, 74.4, 36.2, 32.1, 29.8, 29.5, 29.0, 28.5, 22.8, 14.1. For (b): δ 146.8, 74.4, 36.1, 31.9, 29.4, 29.3, 29.0, 28.5, 22.7, 14.1.

[‡] It was observed that use of 10 mol% of $\text{BH}_3:\text{thf}$ in the hydroboration of dec-1-yne gives similar results. However, we have found it convenient to prepare and use the $\text{BH}_3:N,N$ -diethylaniline complex in these reactions.



Scheme 2. Reagents: i, BH₃:NEt₂Ph (catalyst), RC≡CH; ii, NaOAc/H₂O₂.



Scheme 3. Reagents: i, BH₃:NEt₂Ph (catalyst), RC≡CH; ii, H₂O; iii, I₂/NaOH.

vinylboranes formed by the hydroboration of alkynes with the *N,N*-diethylaniline-BH₃ complex are readily transferred to catecholborane as envisaged in Scheme 1.

We have observed that the reaction of the BH₃:*N,N*-diethylaniline complex with dec-1-yne followed by oxidation with NaOH/H₂O₂ gives only decan-1-ol. Presumably, dihydroboration leading to the formation of the *gem*-dibora derivative takes place under these conditions. The absence of alcoholic products derived from *gem*-dibora compounds in the experiments with catecholborane and *N,N*-diethylaniline-BH₃ indicates that the vinyl transfer reaction to give the alkenyl catecholborane is faster than the formation of the *gem*-dibora compound. Similar results were observed with the reagent prepared by passing B₂H₆ (25 mmol) through a mixture of *N,N*-diethylaniline (1 mmol) and catechol (10 mmol) in benzene at 25 °C.

The stability of the ester group under the present reaction conditions is noteworthy, since catecholborane reduces esters to alcohols at 65 °C.¹² In order to examine whether alk-1-yne can be selectively hydroborated in the presence of alk-1-enes, we employed dec-1-yne (16 mmol) and dec-1-ene (16 mmol) in a synthesis with catecholborane (10 mmol) and *N,N*-diethylaniline-BH₃ (1 mmol), but in this case only 4.5 mmol of decanal was formed besides 2 mmol of decanol. The decanol formed most probably results from the hydroboration of dec-1-ene by BH₃:*N,N*-diethylaniline. Also, an equivalent amount of catecholborane remained unreacted even after 24 h. This rate retardation is not unexpected, since formation of trialkylborane would remove the catalyst 'BH₃' species.

In order to ascertain further the formation of alkenylborane derivatives under the present conditions, we have also carried out the iodination reaction with NaOH/I₂. The alkenyl boronic acid was isolated free of catechol by distilling out the

benzene solvent after hydrolysis. The crude alkenyl boronic acid was iodinated with NaOH/I₂ following a reported procedure.¹³ The corresponding isomerically pure *trans*-alkenyl iodides were obtained in 65–67% yields (Scheme 3).†

We are investigating the use of catecholborane and alkenyl catecholboranes prepared following the procedures reported here. We thank the C.S.I.R. and the D.A.E. for financial support and the U.G.C. for the instrument facilities provided in the form of Special Assistance and COSIST Programmes.

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